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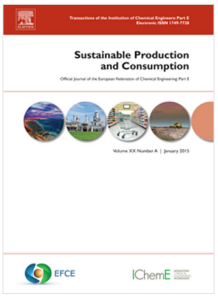

Life Cycle Assessment model for the chlor-alkali process: A comprehensive review of resources and available technologies

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HIGHLIGHTS

- Exhaustive Life Cycle Assessment model to describe the European chlor-alkali sector
- Environmental sustainability of current and emerging electrolysis technologies
- Importance of every life cycle stage is remarked, especially salt production
- Success of emergent technology is challenged by the lack of hydrogen production
- Tool to support decision-making process in the introduction of emergent techniques

Life Cycle Assessment model for the chlor-alkali process: a comprehensive review of resources and available technologies

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ABSTRACT

Currently, the chlor-alkali sector is shared by three main electrolysis technologies: mercury, membrane and diaphragm cell. As the energy demand of the process is one of its main drawbacks, new technological improvements are emerging such as the replacement of the standard hydrogen-evolving cathode in membrane technology by an oxygen-depolarised cathode (ODC). In this sense, the environmental impacts of novel techniques must be analysed over their entire life cycle to assess properly their integration opportunities.

This work develops a life cycle assessment (LCA) model to describe the chlor-alkali European industry. The multi-functional production of chlorine, sodium hydroxide and hydrogen is studied from cradle to gate, including salt production, products treatment and waste management within the system boundaries. While the worst scenario results mercury technique, ODC technology emerges as the most environmentally sustainable

process. The results suggest the importance of considering every process included, especially salt production and brine preparation, which can involve up to 20% of the total environmental impacts. In fact, taken as reference membrane scenario, results demonstrated that the environmental profile can be reduced by up to 18% when lower energy demanding processes for salt production and NaOH concentration were selected. This improvement percentage overcomes the competitive advantage shown by ODC versus membrane technology (7%). This model is a useful tool not only for the comparative assessment of the environmental sustainability of the different chlor-alkali installations, but also to guide and support the decision-making process in the introduction of emergent technologies in the sector.

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KEYWORDS: Life Cycle Assessment, modelling, Chlor-Alkaly industry, membrane technology, oxygen depolarised cathode technology

1. Introduction

The chlor-alkali industry produces chlorine, sodium/potassium hydroxide and hydrogen by the electrolysis of brine. This energy intensive process is the basis for approximately 55 % of the chemical industry in the EU-27 and EFTA countries, as chlorine and sodium hydroxide are basic building blocks for thousands of valuable products. The global chlorine production capacity was estimated at 76.8 Mt in 2012, being a 16% distributed along 75 chlor-alkali plants in the EU-27 and EFTA countries (Brinkmann et al., 2014).

The chlor-alkali sector is a mature industry, in which the mercury cell has been the prevalent technique for many years. Up to the end of the 20th century, the mercury technology dominated in Europe, while the diaphragm technique predominated in the United States and the membrane cell in Japan (Brinkmann et al., 2014). However, this pattern has been evolving since then, as a result of the own restructuring period in which the chlor-alkali sector is immersed to satisfy environmental concerns over mercury and asbestos emissions and market demand. Currently, European mercury installations are being converted or decommissioned, since this process must be phase out by December 2017 (EC, 2013). Obsolete diaphragm plants are also being replaced, since the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation (EC, 2006) prohibits the use of asbestos fibres, although some exemptions are considered.

The membrane cell technique is the state-of-the-art technology in the chlor-alkali industry. Since its introduction in 1970, all new plants, including those built in India and China, are based on membrane cell technique. Nowadays, it represents more than 60% of the total European capacity. Despite reducing the overall energy demand of the

process, energy consumption is still one of the most important issues in this sector (Kiros and Bursell, 2008). A promising approach for reducing the electrolytic energy consumption is the replacement of the common hydrogen evolution cathode by an oxygen depolarised cathode (ODC) (Moussallem et al., 2012). However, only a few examples are currently available: a 20 kt/y chlorine plant in Leverkusen (Germany) that began operating in 2011 by Bayer/UHDE, and a 80 kt/y installation in Shandong (China) sold by Bayer/UHDE to Befar group that started operation in 2015 (Brinkmann et al., 2014). However, this technique requires the use of pure oxygen as raw material and, unlike the rest of technologies, ODC technology does not co-produce hydrogen (Kiros and Bursell, 2008).

Consequently, as the energy consumption of the electrolytic technology is reduced, the impact of other stages such as raw materials extraction and production becomes more significant (Garcia-Herrero et al., 2017). In this sense, the main raw material is sodium chloride, which may be provided by different sources: rock salt from underground deposits obtained by mechanical mining, solar salt obtained by solar evaporation of seawater, brine produced by solution-mining of underground pots and vacuum salt from purifying and evaporating solution-mined brine or dissolved rock salt. Additionally, 70% of the salt employed in the Spanish chlor-alkali industry is sourced from the purification of potash mining waste (Brinkmann et al., 2014). It constitutes an example of circular economy, since it enables the transformation of wastes into a value-added resource.

To assess the integration opportunities of novel techniques in the chlor-alkali business, not only the electricity requirements of the cell itself must be considered but also every life cycle stage. Life Cycle Assessment (LCA) is a widely used tool in process selection, design and optimization to identify clean technologies (Pieragostini et al., 2012).

According to Garcia-Herrero et al. (2017), several works can be found in the literature that study the environmental performance of the chlor-alkali process following an LCA approach. Among them, the European eco-profile provided by Eurochlor (2013) is one of the most complete studies, since it considers every life cycle stage of the current chlor-alkali sector. However, inventory data are not reported and the environmental impacts are shown as industry average values, hindering the comparison among the different technologies and disregarding life cycle stages contribution. Recent studies assessed the environmental sustainability of the ODC technology, discussing the influence of the lacking hydrogen co-production. Jung et al. (2013) reported a preliminary comparison between membrane and ODC technologies, although raw material preparation and product treatment are neglected. The same authors extended this work later (Jung et al., 2014), assessing seven impact categories and including NaCl extraction and NaOH treatment. Despite stage contributions are shown, different NaCl sources are not compared and brine preparation and chlorine treatment are not included. Same life cycle stages are considered by Kätelhön et al. (2015), which estimated the global impact intensity of mercury, diaphragm, membrane and ODC. The novelty of this work is the study of the potential market introduction of ODC technology. However, it lacks from a proper NaCl extraction, production and brine preparation description as Jung et al. (2014). Chlorine treatment is as well not included. Conversely, a more detailed study is conducted by Hong et al. (2014), albeit it is focused only in the electrolytic production of sodium hydroxide in China, being its representativeness limited. Therefore, there is a gap in the literature regarding the environmental sustainability of the current and emergent techniques across their entire life cycle, considering not only the electrolytic stage but also raw materials extraction and preparation (including salt production and brine preparation) and products treatment.

In a previous work (Garcia-Herrero et al., 2017), we focused on the electrolytic technologies using the same salt source (i.e. solution-mining brine) for comparison purposes. This paper aims at developing a comprehensive LCA model of the European chlor-alkali industry, so that any possible scenario can be described. Every life cycle stage is included, making a special effort in the description of the different salt mining and brine preparation options. Additionally, the environmental impacts of the current (i.e. mercury, diaphragm, membrane) and emergent technologies (ODC) are assessed from cradle to gate, considering different salt sources (KCl waste, vacuum salt and solution mining brine) and products treatment according to the electrolysis technology and plant location. Hence, this model provides a complete overview to asses multiple chlor-alkali scenarios, but also to inform interested stake-holders and support decision-making processes about the integration opportunities of the emergent ODC technology in the chlor-alkali business.

2. Methods

This work is conducted following the requirements of ISO 14040/44 guidelines (ISO, 2006a; ISO, 2006b). According to them, LCA methodology consists of 4 stages: (i) definition of the goal and scope of the study, (ii) life cycle inventory analysis, (iii) life cycle impact assessment and (iv) interpretation.

2.1 Goal and scope

This study develops a LCA model able to describe the chlor-alkali industry, with the aim of assessing the environmental sustainability of the process and the integration opportunities of emergent technologies in the sector. The model encompasses the

detailed analysis of the production of chlorine and the corresponding co-production of sodium hydroxide and hydrogen. The chlor-alkali electrochemical process generates in a fixed ratio 1 ton of chlorine, 1.128 ton of sodium hydroxide and 28.5 kg of hydrogen, being this mixed ton named electrochemical unit (ECU). As the production of the three products cannot be controlled independently, the ECU is considered as functional unit, which is the quantitative reference for which the inputs and outputs of the process under study are related (ISO, 2006b). Therefore and for comparison purposes, it is necessary to expand the functional unit in ODC system to include hydrogen production by system expansion, since this technology does not manufacture hydrogen (Jung et al., 2014). A further discussion about the functional unit selection in other works is available in Garcia-Herrero et al. (2017).

As the focus of the work is on the production process, the scope of the study is from 'cradle to gate'. In this sense, salt production, waste and secondary products recycling, raw materials transportation, treatment stages for products conditioning and waste streams and emissions management are considered within the system boundaries.

Sodium hypochlorite is always present in every chlor-alkali plant. However, as its production is often minimise, no significant environmental burdens are attached to its generation. Almost every existing plant and nearly all new implementation projects consider a vacuum dechlorinating stage for brine, which enables the valorisation of the chlorine recovered and avoids sodium hypochlorite production. For this reason, the production of sodium hypochlorite is outside the scope of this work. The impacts from construction of major capital equipment and from the maintenance and operation of support equipment were also excluded, as its contribution is typically negligible owing to the long lifetimes of industrial installations.

Within the system boundaries, the process is divided into 4 subsystems to identify easily

the contribution of each stage (Fig. 1). Due to the flexibility conferred to the model, practically all the chlor-alkali possible scenarios can be described using this approach.

- Subsystem 1: Salt mining. Given the wide range of salt qualities employed as raw material in this process and the different environmental impacts attached to them, the consideration of this individual subsystem is fundamental. Rock salt, solar salt, vacuum salt, salt from KCl waste and brine from solution mining are the five salt processes under consideration. Transportation from its manufacture to the chlorine installation is also included in this subsystem. The inputs to this subsystem are energy, water and raw salt, as well as reactants when required for pretreatment. The outputs of the system are the salt product and the effluents, air emissions and solid waste.

- Subsystem 2: Brine preparation. The chlor-alkali process requires sodium chloride as an aqueous solution of salt (i.e. brine). The quality requirements can vary as a function of the electrolytic technology under study. On the one hand, the environmental impact of this stage may be subjected to the presence of impurities related to the quality grade. On the other hand, the configuration of the brine purification stage is also a significant issue to consider in the chlor-alkali production. Two different configurations can be distinguished: (i) brine recirculation circuit (i.e. close circuit), where the depleted brine is resaturated with solid salt and (ii) once-through brine system (i.e. open circuit), which is typical of installations using solution-mined brine. Both configuration are integrated in the model. For all the technologies under study, a primary purification system based on impurities precipitation is considered. An additional secondary system based on ion-exchange resins is assumed for the technologies that need further purification.

- Subsystem 3: Electrolysis. The current and emergent technologies in the chlor-alkali sector are considered in this subsystem. Thus, separate models for mercury, membrane in bipolar and monopolar configuration, diaphragm and ODC technology are included in this stage. The system inputs are energy, water and raw materials requirements, while the outputs are represented by the three products manufactured and the emissions to air and solid wastes to manage. All the flows are characterised to describe the corresponding technologies.

- Subsystem 4: Products treatment. Before being sent to the end user, the products from the electrolysis require further treatment. In some cases, treatment processes are determined not only by the product to purify, but also by the electrolytic technology. Hence, specific treatment models are created for each product according to the corresponding technology. Regarding chlorine conditioning, a single common process is needed. Conversely, the treatment process for sodium hydroxide depends on the nature of the electrolytic technique due to the different product quality delivered for each technology. The inputs of the subsystem are energy consumption, water and raw materials. The system outputs are the conditioned products ready to distribution and utilisation, the aqueous effluents and the emissions to air and solid wastes to manage. Hydrogen treatment is not considered for ODC technology, as it is not produced in the electrolysis. Furthermore, the treatment processes of NaOH and hydrogen delivered by mercury technique take into account the presence of mercury.

2.2 Scenarios description

Considering these subsystems, numerous scenarios can be suggested. Despite any combination of subsystems can be described, the selected scenarios may be debatable

and likely to generate a deeper analysis about the chlor-alkali business. In particular, this work is focused on the 5 scenarios described in Table 1. The main difference among them, is the electrolytic technology assumed: mercury (S1), bipolar membrane (S2 and S3), diaphragm (S4) and ODC technology (S5). As can be observed, bipolar membrane is depicted by both S2 and S3 scenarios. This is because while the latter describes the best available technology, the former integrates the most sustainable processes for salt production and NaOH concentration. Another important difference among these scenarios is the source of salt used as raw material. Further detail can be found hereafter.

- S1: mercury scenario. In this technology, the electrolysis cell is slightly inclined, and the film of mercury flows along the bottom together with the brine. A 10 KA/m^2 current density is assumed to be supplied to the cell, which decomposes the brine liberating chlorine gas and metallic sodium (Arcega et al., 2011). As opposed to the rest of electrolytic technologies, there is no physical barrier dividing the cell into two compartments. The sodium reacts with mercury to form an amalgam that flows from the electrolytic cell to a separate reactor, called decomposer (Brinkmann et al., 2014). There, the amalgam reacts with water producing NaOH (50%) and hydrogen. Despite the fact that mercury technology must be phase out by the end of 2017 (EC, 2013), it still represents a 19.7% of European sharing (Eurochlor, 2016). The largest capacity is located in Spain, depicting an 81% of national capacity. Since 70% of the sodium chloride used in Spanish plants is obtained by purification of NaCl-containing wastes from the mining of potash (KCl), this is the salt source assumed for this scenario. Salt is considered to be transported 50 km by train. An 80% valorisation rate is considered for hydrogen.

- S2: membrane scenario A. This scenario sets out membrane technology. Anode and cathode compartments are divided by an ion exchanger membrane. The brine flows along the anodic compartment, where chlorine ions are oxidized to chlorine gas. Sodium ions in water migrate through the membrane to the catholyte, where a sodium hydroxide solution is located. Water is hydrolysed in the cathode, liberating hydrogen gas and hydroxyl ions. Sodium and hydroxyl ions are combined to form sodium hydroxide (typically ca. 33%). It is a bipolar membrane operating at high current density (5 KA/m^2), which represents de non-maximum operating conditions. Same considerations as in S1 are assumed for salt source and transport, as well as hydrogen valorisation rate. Regarding the brine circuit, a secondary purification stage is included, as membrane technique requires more purified inputs than mercury technology. A 3 effects evaporation process is considered for NaOH treatment, which besides the selection of KCl waste as salt source, constitutes the less energy demanding combination for membrane scenario.

- S3: membrane scenario B. This scenario represents a modification of S2. In this case, a different salt source is considered. Vacuum salt obtained from rock salt is selected as raw material, since it is the most common used in Europe. At the same time, this enables to assess the environmental impacts of salt production within the life cycle of the chlor-alkali process. A 2 effects technique is assumed for NaOH concentration. In contrast to S2, this scenario is aimed to describe a system that uses the best available technology but whose environmental sustainability may be degraded by other stages process selection.

- S4: diaphragm scenario. In this electrolytic technique, the diaphragm separates the feed brine from the solution of NaOH present in the cathode. The purified

brine enters the anode chamber and percolates through the diaphragm into the cathode compartment (Brinkmann et al., 2014). Chlorine is generated in the anode, while NaOH (12%) and hydrogen are directly produced in the cathode. In this case, the brine is pumped the same distance that the rest of scenarios. Diaphragm technology always uses a once-through system to purify the brine, most commonly using solution-mined brine and thus selected as salt type for this scenario. Only the primary brine treatment is required (Brinkmann et al., 2014). The cell is assumed to be supplied with a high current density (4 KA/m^2). This scenario considers the recovery of condensates and salt from the 3 effects caustic evaporators, which are reincorporated to the brine supply.

- S5: ODC scenario. This scenario represents the emergent technology. It is based on the replacement of the standard hydrogen-evolving cathodes employed in membrane technology by oxygen depolarised cathodes that reduce the oxygen to produce hydroxide, instead of converting water into hydrogen and hydroxyl ions. This modification reduces the electricity consumption around 30% with regard to membrane cell technique (Lakshmanan et al., 2014). Since the ODC technology suppliers announces the use of same membranes as in bipolar technology, it could be assumed that it is also possible to combine with salt from KCl waste. However, ODC has to meet strict requirements for successful operation (Brinkmann et al., 2014) and the use of KCl waste may lower the lifetime of the membrane owing to its low quality. Therefore, given such reasons are being limited this salt type to the Spanish region, it has been considered that the comparison of bipolar and ODC technology with vacuum salt could be more interesting for stakeholders. The brine circuit configuration is identical to scenarios S2 and S3. A 6 kA/m^2 current density is assumed as it is the suggested

by the technology suppliers and is comparable to the other scenarios. A 3 effects evaporation is considered for comparison purposes to S3. Unlike the rest of technologies, this technique does not produce hydrogen which could otherwise be used in chemical reactions or to produce steam and electricity via combustion or fuel cells.

Table 1 Description of the systems under study

	Salt type	Salt transport	Brine circuit	Electrolytic technology	Current density (KA/m^2)	NaOH concentration	H_2 recovery
S1	Salt (KCl)	50 km, train	Close	Mercury	10		80%
S2	Salt (KCl)	50 km, train	Close + secondary purification	Bipolar membrane	5	3 effects	80%
S3	Vacuum salt	50 km, train	Close + secondary purification	Bipolar membrane	5	2 effects	80%
S4	Brine	50 km, pumping	Open	Diaphragm	4	3 effects	80%
S5	Vacuum salt	50 km, train	Close + secondary purification	ODC	6	2 effects	

2.3 LCA model and LCI inventory

High quality data is essential to make a reliable evaluation in an LCA analysis, and this step requires a lot of time and effort (Bacenetti et al., 2013). Primary data were mostly gathered from the Best Available Techniques (BAT) Reference Document (or BREF Document) for the production of chlor-alkali (Brinkmann et al., 2014). An 86% of the chlor-alkali operating installations are covered by this document. The rest of primary

data are collected from bibliographic sources and mass balances. Background data, such as energy production processes, tap water production or waste management processes, were collected from the PE International database using GaBi 6.0 software for the LCI modelling (PE International, 2014). Further information about the main data sources, the temporal framework and geographical representativeness of the data are shown in Table S1 in the supporting material (SM).

LCA models are cost-effective tools for the evaluation of multiple scenarios and the definition of best environmental performance processes (Corominas et al., 2013). The LCA model is divided into the 4 subsystems previously described, as shown in Fig. 1. In this subsection, assumptions for input and output flows are detailed for each system. More details on the description of the subsystems under study are available in sections S1-S2 of the supporting material (SM), where the flow diagrams and LCI data of the subsystems under study are outlined.

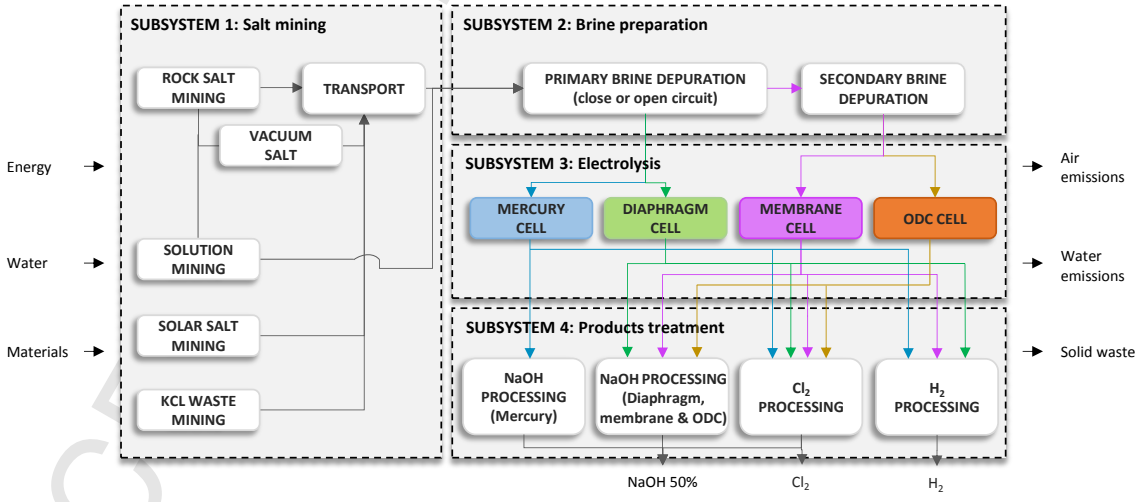

Fig. 1 Flow diagram comprising the subsystems under study: salt mining, brine preparation, electrolysis and products treatment.

2.3.1 Salt mining

Solid salt is usually the basic raw material, which refers to rock salt, solar salt and vacuum salt. Rock salt is produced by mechanical mining in underground deposits, delivering a 93-99% salt quality. Solar salt is obtained by solar evaporation of seawater or brine. In this case, mineral materials are often separated by fractional crystallization, providing a nearly 99% NaCl purity (Brinkmann et al., 2014). Generally, every salt type can be used for vacuum salt production. However, it is mainly obtained from rock salt processing. The brine is purified to remove calcium, magnesium and sulfate impurities. Multiple effect evaporators and mechanical steam recompression are the main recovery technologies, which deliver a 99.5% content of NaCl (Feldman, 2005).

Salt can also be used in the form of solution-mined brine, which is obtained by forcing water or weak brine into the rock salt deposit to convert it into a concentrated solution and bring it back to the surface (Brinkmann et al., 2014). A lower quality is expected for this salt. In Spain, salt is usually sourced from the purification of NaCl-containing wastes provided by the mining of potash (KCl), including wastes from historic landfills.

The compositions from different sources vary widely but the main impurity in nearly all salts is some form of calcium sulphate. Table S2 in the SM shows the composition assumed for the different types of salt. Furthermore, Table S3 outlines the main inputs and outputs of the scenarios under study for this subsystem, which are compiled and estimated using the LCA model described below.

Materials consumption

A pretreatment stage is included for vacuum salt, considering the consumption of sodium carbonate and sodium hydroxide (Fig. S1 in SM). Regarding salt from KCl waste, it is assumed that none material is consumed in its production, as this raw

material is in fact a waste delivered by another production process.

Energy consumption

Energy data for rock salt are sourced from Goetfried et al. (2012), where mining facilities from Heilbronn (Germany) are taken as reference of this salt type. In global terms, values from these installations are representative of the European average. Solar salt requirements of energy are also obtained from Goetfried et al. (2012), where the electric specific consumption is reported for a facility located in Western Australia. The data are again assumed to be comparable to those from European plants. Regarding vacuum salt, state of the art data for multiple-effect evaporation and mechanical steam recompression are considered (Westphal et al., 2010). Data from the chlor-alkali sector are taken as reference for describing the production of salt from potash mining wastes (ANE, 2010).

The energy requirements for the production of solution-mined brine (E) is modelled considering both the energy consumed in solution mining (E_S) and the energy requirements for transportation to the chlor-alkali plant (E_T) as:

$$E = E_S + E_T \quad (1)$$

The former depends on the plant capacity and mining design. The energy consumption in the extraction wells is a function of the pressure requirements. Hence, the pressure needed for solution mining is estimated using the design data of the installation (casing, tubing) and the plant capacity (F, m^3/h) as described in Table 2.

Table 2 Mathematical expressions for the calculation of pressure requirements for solution mining

Mining characteristics			
Casing (cm)	Tubing (cm)	Pressure estimation, P (bar)	
15	9	$12.5 \cdot \exp\left(8.60 \cdot 10^{-3} \cdot F\right)$	(2)
20	11.5	$11.9 \cdot \exp\left(4.50 \cdot 10^{-3} \cdot F\right)$	(3)
25.4	16.5	$11.7 \cdot \exp\left(2.20 \cdot 10^{-3} \cdot F\right)$	(4)

Then, the pressure loss is determined to estimate the hydraulic power required for brine pumping, as shown in section S3 in the SM. An 85% pump efficiency is assumed.

The second term of expression (1) describes the pipeline transport of the solution-mined brine to the chlor-alkali facilities (E_T). It depends on the pressure drop produced along the pipe, which is assumed to be due to the frictional effect of the fluid near the surface of the pipe. The pump requirements are then estimated using the fanning factor and the pipe specifications. More information can be found in section S3.

Water consumption

Data of water usage for every salt type are sourced from the literature (ANE, 2010; NYSDEC, 2015; Sedivy, 2009). An exception is found for vacuum salt, whose water consumption is modelled considering the water requirements for reactants conditioning. Among them, it is particularly important the presence of NaOH in excess to ensure the efficiency of the precipitation reactions needed to achieve the desired salt quality. Thus, it is assumed that the concentration of NaOH is maintained around 300 ppm.

Liquid effluents

A purge flow is integrated in the corresponding vacuum salt subsystem to maintain the sulphate concentration in the circuit. This effluent contains mainly chlorine, owing to

the saturated nature of the brine, as well as sulphate and other minor impurities. In practice, the purge flow is reduced, as not the entire amount of sulphate contained in the rock salt is diluted (O'Brien et al., 2007). A 50% dissolution of the sulphate present in the raw salt is assumed in this work. Hence, the content of salt (%) and water (kg/t salt) in the purge can be determined as follows:

$$[Salt]_{purge}(\%) = 20.6 \cdot [SO_4^{2-}]^{0.8} \quad (5)$$

$$[H_2O]_{purge} = \frac{Salt_{purge}(\%) \cdot 10 \cdot [H_2O]}{[NaCl]} \quad (6)$$

Where $[NaCl]$ and $[H_2O]$ are 250 g/kg and 750 g/kg, respectively.

As well as for water input, the rest of liquid effluents are characterised according to the literature (ANE, 2010; Mustafa Alaa and Abdullah, 2013).

Solid waste

Solid waste from vacuum salt production is estimated according to the rock salt impurities entering the subsystem. The waste is generated both in the dissolution and purification stages mostly as a result of calcium and magnesium precipitation.

Therefore, the solid waste generated (kg/t salt) can be calculated as a function of the impurities (i.e. calcium, magnesium and sulphate input, kg/t salt) in the system:

$$A_bB_{a_{out}} = \frac{A^{a-}{}_{in} \cdot M_{A_bB_a}}{M_A \cdot NaCl_{salt}(\%)} \quad (7)$$

Where M is the molar mass of the corresponding elements and compounds (i.e. $CaCO_3$, $Mg(OH)_2$, $CaSO_4$) and $NaCl_{salt}(\%)$ is the purity of the salt employed as raw material expressed as a decimal value. The rest of solid waste flows are described following reported data (ANE, 2010; Baseggio, 1974).

2.3.2 Brine preparation

The quality of the raw material and the brine quality requirements for each technology determine the complexity of this process. After salt mining, brine is purified in a process that consists of a primary system common to the four technologies (Fig. S2 in SM). It is based on precipitation and filtration to reduce the impurities concentration that could affect the electrolysis. These undesirable components are mainly sulphate anions, calcium and magnesium anions and metals, which can precipitate inside the membrane or diaphragm and promote hydrogen formation in mercury cell.

An additional secondary system is needed for the membrane (and ODC) cell technique to maintain a high-level performance. Calcium and magnesium reduction in the previous process is not enough and thus a softening step is required. Generally, it is based on polishing filtration and further purification using ion-exchange resins.

Regarding the type of salt source, the brine employed in mercury and membrane installations is usually obtained by dissolving solid salt in the depleted brine from constant recycle (Brinkmann et al., 2014). Conversely, diaphragm plants always use solution-mined brine in open once-through circuits, which often consider the recirculation of salt recovered from caustic evaporators.

The LCI data for the processes related to brine preparation are displayed in Table S4 in the SM, while further detail for LCA modelling is described as follows.

Energy consumption

The contribution of the driving force for brine circulation is below 5% of the total energy consumption. Thus, a steel rule is applied and the driving force is not considered for either the open or the close system. Conversely, the thermal requirements for

secondary purification are included, as brine must be preheated to 65ºC for ion exchange resins performance.

Water and salt consumption

These two input flows depend on the electrolytic technology under study, which determines the working capacity. Regarding the once-through brine system, feed flows of 13, 12 and 14 m^3 per ton of chlorine are assumed for mercury, membrane/ODC and diaphragm technologies, respectively. Conversely, a 20 m^3/t Cl_2 flow is considered for close circuit. The main difference between both configurations is that the depleted brine leaving the electrolyser turns into an effluent when the once-through system is considered.

Reactants consumption

Three main reactants are consumed in this subsystem: sodium carbonate, sodium hydroxide 25% (required for calcium and magnesium precipitation) and hydrochloric acid 32% (used for pH adjustment in electrolysis and dechlorination steps).

Effluents

For the once-through system, the effluent is the entire stream leaving the mercury or the membrane/ODC cells. The same is not applied to diaphragm technology, where the brine and the sodium hydroxide leave simultaneously the electrolytic cell. This stream enters the concentration process, where the solid salt is recovered, as well as the condensates from this step. Hence, no effluent is considered for the diaphragm system. Liquid effluents for close systems are described using equations (5) and (6).

A desulphation step is included in some chlor-alkali plants to minimise the brine purge. This step is not considered in the LCA model as it is not a widespread practice.

Regarding secondary purification, which is essential in membrane/ODC scenarios, the

resins regeneration process includes the consumption of low concentrated hydrochloric acid and sodium hydroxide. The diluted brine stream generated is typically neutralised and recirculated back to the system. Thus, only in vacuum salt scenarios is considered an effluent, as it is used for the purge of calcium and magnesium. Due to the high vacuum salt quality, no sulphate purge is needed.

Solid waste

As was previously described for the salt mining subsystem, the precipitation of impurities generates solid waste, which is described by expression (7)). In the model, waste is disposed of in a landfill site.

2.3.3 Electrolysis

This is the main stage of the process. It is based on the supply of electric energy to the cell, where the sodium chloride in solution is decomposed because of the potential difference established between the two electrodes. Chlor-alkali products are then obtained according to (8).

$$2NaCl + 2\,H_2O \rightarrow 2\,NaOH + H_2 + Cl_2 \qquad (8)$$

At the anode, chloride ions are oxidised to generate chlorine following the same reaction in all the technologies (9):

$$2\,Cl^- \rightarrow Cl_2 + 2\,e^- \qquad (9)$$

Conversely, the cathode reaction depends on the technique under study. In the mercury cell, a sodium/mercury amalgam is formed and hydrogen and hydroxide ions are obtained from the reaction of the amalgam with water (10)-(11).

$$Na^+ + e^- + Hg_x \rightarrow Na - Hg_x \quad (10)$$

$$2\,Na - Hg_x + 2\,H_2O \rightarrow 2\,NaOH + H_2 + 2\,Hg_x \quad (11)$$

Regarding membrane and diaphragm cell techniques, water is directly decomposed to generate hydrogen and hydroxide ions at the cathode (12).

$$2\,Na^+ + e^- + 2\,H_2O \rightarrow 2\,NaOH + H_2 \quad (12)$$

Conversely, hydrogen is not co-produced when ODC technology is employed (Moussallem et al., 2008). In this case, oxygen is also required as raw material, leading to the cathodic and overall reactions described in (13) and (14), respectively (Morimoto et al., 2000).

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \quad (13)$$

$$2NaCl + O_2 + 2\,H_2O \rightarrow 4\,NaOH + 2\,Cl_2 \quad (14)$$

The flow diagram of this subsystem and the main inputs and outputs are detailed in Table S5 and Fig. S3 in the SM, respectively. The main assumptions and data sources are explained below.

Energy consumption

In common electrolysis cells, low current densities involve moderate electric specific consumptions. However, this also means that a higher amount of electrolysers are required, which results in larger investment and maintenance costs for same chlorine production. Chlor-alkali plants often work under variable current densities, which depends on product demand and energy price fluctuations. Energy consumption in this subsystem is a function of the process under study. The relationship between the mentioned variables for the technologies under study, are modelled according to Schmittinger (2008) and UHDE (2015). A 95% efficiency in current density is assumed.

Regarding ODC technology, not enough performance data are available in the literature to be expressed as a mathematical function. Current designs operate under 4 kA/m^2 current densities, reporting energy consumptions of 1460 kWh/t NaOH. Values of 6 KA/m^2 and 1600 kWh/t NaOH are also announced (Hofmann et al., 2012). The latter is assumed in this model to describe a system as comparable as possible to the rest of scenarios. The German grid mix is considered for this technology.

Water consumption

Two different sources of water consumption are distinguished in this subsystem. The first is referred to the reaction itself. To produce hydrogen and sodium hydroxide in the electrolysis, 0.51 $m^3/t\ Cl_2$ of water is required according to the stoichiometric ratio. The second consumption point is the use of water as solvent for the production of sodium hydroxide. The water quantity varies according to the typical sodium hydroxide purity delivered by each technology. Within the consumption of water, the variable percentage of condensates recovery from the NaOH concentration step is also considered. This is integrated in the diaphragm, membranes and ODC models.

Reactants consumption

The stoichiometric sodium chloride required in the electrolysis is 1.65 t NaCl/t Cl_2. NaCl losses through the effluent purge are also taken into account. In addition, pure oxygen requirements are considered for ODC scenario, which are estimated at 0.25 ton of O_2 per ton of Cl_2.

Effluents

The effluents obtained in this subsystem are related to the previous brine preparation process. However, to distribute environmental burdens according to their sources, emissions caused in the electrolysis are considered as an output of the system, although they come out with brine effluent. Hence, emissions to water of free chlorine, chlorate and bromate are included. Mercury emission is also taken into account in mercury scenario.

Emissions to air and solid waste

Emissions to air include chlorine for every scenario and also mercury for the specific mercury technology. The average mercury emission data claimed by European plants is considered in this study.

Regarding solid waste, mercury and asbestos (if used) are the specific solid outputs of mercury and diaphragm technologies, respectively.

2.3.4 Products treatment

Products

Chlorine, sodium hydroxide and hydrogen are the three common products manufactured by the currently industrial technologies. However, the features of the different products depend usually on the technology applied, which involves further specific treatment.

The main characteristics of chlor-alkali products according to the technology employed and LCI data are gathered in Table S6 in the SM. A different situation is observed for

ODC, as hydrogen is not co-produced. Hence, same composition for NaOH and chlorine as in membrane technology is assumed.

Reactants consumption

Chlorine conditioning, which is a common process for every scenario under study, consists of a dry step using concentrated sulfuric acid. Regarding the treatment of sodium hydroxide and hydrogen obtained from mercury technology, a demercuration step using active carbon is needed.

Energy consumption

A NaOH concentration step is required in diaphragm, membrane and ODC scenarios. The energy consumption varies according to the number of concentration effects.

Liquid effluents

In chlorine treatment process an output flow containing sulphuric acid diluted to 60% and proportional to the input is defined. A system expansion is conducted to describe the consumption of this acid as raw material for another process, avoiding thus the environmental impacts related to this effluent (Fig. S4 in SM). Regarding hydrogen process, no effluent is considered as output. However, the model addresses the option of caustic condensates non-recovery due to quality problems. A variable describing the recovery percentage is modelled. The unrecovered condensates are considered as an additional effluent, which directly affects the water consumption of subsystem 3.

Air emissions

The hydrogen that is not valorised is included in the system as an emission to air. As for condensates recovery, this process is modelled using a variable that describes the valorisation rate, which confers flexibility to the system. Regarding hydrogen treatment

in mercury technology, the emission of residual mercury from the demercuration process is also considered.

Solid waste

Active carbon is required in mercury technology for the demercurisation of both NaOH and hydrogen. This carbon turns into waste once it achieves its maximum adsorption capacity. The carbon specific consumption and carbon waste were estimated based on the sulphur content of commercial active carbon. The recovery of mercury by distillation of this solid waste has been assumed at 95%.

2.4 Allocation and avoided burdens procedures

Chemical industry processes are often multifunctional processes, as they present more than one output of valuable products and co-products. Such is the case of the chlor-alkali process, where chlorine, sodium hydroxide and hydrogen are co-produced (Eurochlor, 2013). To handle multi-functionality, allocation should be avoided whenever possible, applying system expansion instead. This approach is performed by including the additional functions related to co-products, which involves the subtraction from the system under study of the environmental impacts of the alternative process to generate the equivalent co-product amount. Hence, the system is 'compensated' by the avoided burdens related to the additional function (Weidema, 2001). However, system expansion should only be applied when there is a dominant, displaced product and when there is a dominant, identifiable production path for the displaced product (PlasticsEurope, 2011). Otherwise, allocation procedure is used.

The majority of industrial processes are designed to optimise their economic profitability. Hence, the revenues from the products are often taken as criteria for the

distribution of process inputs and outputs over the co-products (i.e. allocation). Nevertheless, once it is industrially implemented, process performance is essentially determined by technical features. Therefore, economic allocation seems to be inadequate (Boustead, 2005).

Since the functional unit was defined as the combined production of chlorine, sodium hydroxide and hydrogen, system expansion is conducted in ODC scenario to include the lacking hydrogen production. More than 80% of the hydrogen produced as primary product (not as by product) is produced using steam reforming of natural gas and thus this process has been chosen for the system expansion procedure. (Jung et al., 2013; Kätelhön et al., 2015). Finally, mass and economic allocation were compared.

2.5 Life Cycle Impact Assessment

The Life Cycle Impact Assessment (LCIA) methodology applied in this study, which follows the Environmental Sustainability Assessment (ESA) procedure developed by Margallo et al. (2014). In particular, the metrics proposed are based on those from the Institution of Chemical Engineers (IChemE, 2002). The indicators, which provide a balanced framework of the environmental impacts related to inputs and outputs to the process, are described by the consumption of natural resources (NR) and the environmental burdens generated (EB) (García et al., 2013). The former is integrated by the usage of energy ($X_{1,1}$), materials ($X_{1,2}$) and water ($X_{1,3}$). The EB metric represents the environmental burdens to air ($X_{2,1}$), water ($X_{2,2}$) and land ($X_{2,3}$) compartments. Regarding EB to air, the following impact categories are considered: atmospheric acidification (AA), global warming (GW), human health (carcinogenic) effects (HHE), stratospheric ozone depletion (SOD) and photochemical ozone formation (POF). EB to

water is described by aquatic acidification (AqA), aquatic oxygen demand (AOD), ecotoxicity to aquatic life (metals to seawater) (MEco), ecotoxicity to aquatic life (other substances) (NMEco) and eutrophication (EU). Finally, EB to land gathers the amount of generated hazardous and non-hazardous waste.

However, the main problem attached to these set of metrics is that they are measured in different units, which difficult the decision-making process. In this sense, normalisation relates the characterisation results to reference values (Finnveden et al., 2009), simplifying the comparison among the different impact categories.

The consumption of NR (X_1) differs at each plant. Hence, to ascertain if the consumption of a plant is reasonable and to establish a comparison among the different plants, a valid reference should be used. The average consumption of the European chlor-alkali technologies according to its level of implementation in 2014 (23% mercury, 62% membrane, 15% diaphragm) is used as reference for internal normalisation ($X^{ref}_{1,i}$) (Eurochlor, 2015).

Conversely, an external procedure is applied to normalise EB, since each impact category is measured in different units. The threshold values stated in the European Pollutant Release and Transfer Register regulation (E-PRTR, 2006) are used for this purpose ($X^{*}_{2,j,k}$) and considered as weighting factors to obtain the dimensionless impacts indicators (Table S7 in the SM). These values provide a general outlook of the environmental situation of the plant at a European level (Irabien et al., 2009). Accordingly, NR and EB can be normalised as described in (15) and (16).

$$X^{*}_{1,i} = X_{1,i} / X^{ref}_{1,i} \quad (15)$$

$$X^{*}_{2,j,k} = X_{2,j,k} / X^{ref}_{2,j,k} \quad (16)$$

Where *i* represents different NR (energy, materials and water), *j* represents each environmental compartment (air, water and land), *k* designates the environmental impacts to each compartment and $X^{*}_{1,i}$ and $X^{*}_{2,j,k}$ are the normalised values of $X_{1,i}$ and $X_{2,j,k}$, respectively.

To establish a complete overview of the environmental performance of the process, the dimensionless variables are subjected to a weighting procedure. Weighting represents the assignment of importance coefficients to the different impact categories for their aggregation into a single index (Rowley et al., 2012). The 3 normalised NR and the 12 normalised EB variables are aggregated according to (17) and (18) to obtain the composite NR indicator (X_1) and the EB indexes to air ($X_{2,1}$), water ($X_{2,2}$) and land ($X_{2,3}$):

$$X_1 = \sum_{i=1}^{i=n} \alpha_{1,i} X^{*}_{1,i} \qquad n \in [2,3] \qquad (17)$$

$$X_{2,j} = \sum_{j=1}^{j=m} \beta_{2,j,k} X^{*}_{2,j,k} \qquad m \in [1,2] \qquad (18)$$

Where $\alpha_{1,i}$ is the weighting factor for energy, materials and water variables; $\beta_{2,j,k}$ is the weighting factor for EB. Consequently, the NR index depends on the weights assigned to each final resource. In particular, an equally relevance is assumed for the 3 NRs, which involves a $\alpha_{1,i}$ =1/3 for each *i*. This is assumed because it is the clearest way to obtain a single index that allows a comparison across several systems (Margallo et al., 2014). This provides a simplified description of the environmental behaviour of the process, requiring the assessment of the individual NR to determine the critical process points. Other weighting methodologies are possible and may be further discussed.

3 Results and discussion

3.1 Natural resources

The NR indicator includes the usage of energy, materials and water as final useful resources for the different scenarios under study. The variable energy ($X_{1,1}$) considers the consumption of electricity, steam, diesel and natural gas. The consumption of salt, which is a common raw material for all the scenarios, is included in the utilisation of materials ($X_{1,2}$). This value also considers the reactants needed for brine preparation and products treatment, such as sodium carbonate, NaOH 25%, HCl 25% and active carbon. It must be highlighted that, unlike the rest of scenarios, ODC technology requires pure oxygen as reactant and does not produce hydrogen. Hence, both contributions are taken into account for S5, being the latter included by system expansion for comparison purposes. Finally, the consumption of water ($X_{1,3}$) gathers the water requirements for salt mining, brine preparation and other stages.

The normalised NR results compared to the European reference are gathered in Fig. 2. As was observed in our previous work (Garcia-Herrero et al., 2017), mercury cell technique (S1) is the less environmentally sustainable scenario, followed by diaphragm technology (S4). Both are over the European average for most of the categories. This is mainly due to the energy requirements of the electrolytic cell, which are responsible for nearly 99% of the total energy usage in S1. This is in agreement with other studies, as an example Eurochlor (2013), where although results are not shown for each separated technology, it states that mercury technology requires more electric energy for electrolysis than the rest of techniques. As was also expected, the referred contribution losses importance for S4 (87%), as opposed to the high amount of thermal energy necessary for sodium hydroxide concentration.

However, scenario S3, which describes the current best available technology and is

recognised by its energy intensity reduction, only presents a 13% energy reduction with regard to S1. Furthermore, it must be remarked that this study is focused on bipolar membrane configuration. In this sense, the use of monopolar configuration could lead to higher energetic requirements and thus the competitive advantage of this scenarios would be further reduced.

The less energy demanding scenario is S2, which is also based on membrane cell technology. The main difference of this process with regard to S3 is that it integrates the most energetic sustainable options regarding salt mining and NaOH concentration. This involves a 17% reduction of primary energy consumption with regard to S3.

An intermediate situation between S2 and S3 is observed for the emergent ODC technology. Despite its decrease in the electricity dependency of the electrolytic stage, two additional sources of energy consumption must be considered: the production of oxygen and hydrogen. Consequently, this scenario only represents a 7% reduction with regard to S3 and a 12% increase regarding S2.

Similar conclusions can be drawn for the usage of materials and water. In addition to the previously described contributions, it must be considered the related consumption of materials and water for primary energy production. In fact, the energy demand is the crucial factor influencing these results.

However, what is important to highlight in this work, is that salt mining stage is not a negligible process and present important impacts often disregarded in the literature. For example, vacuum salt production is the less sustainable salt source and accounts for around 17% of the total energy demand in S3 and S5. Conversely, the processes using salt from KCl waste are benefited from the zero burdens approach that is assumed for the use as raw material of another process waste. This involves an almost negligible contribution of salt mining to energy, materials and water consumption in S1 and S2.

Additionally, it is reflected the reduced improvement that S3 provides against S1 when the best environmentally sustainable salt source is assumed for the former and the less for the later. In particular, this difference between S1 and S3 is below 2% when the consumption of materials is assessed. On the other hand, the contribution of brine preparation remains below 5% for every category and technology, which was also observed in our previous study (Garcia-Herrero et al., 2017). However, the fact of using a close circuit instead of a once-through system to purify the brine, involves a reduction in the consumption of raw materials (i.e. salt) as can be inferred from the comparison of both works. This is only extensive to S1 and S2, since salt mining stage for S3 and S5 is significantly influenced by the consumption of materials for primary energy production.

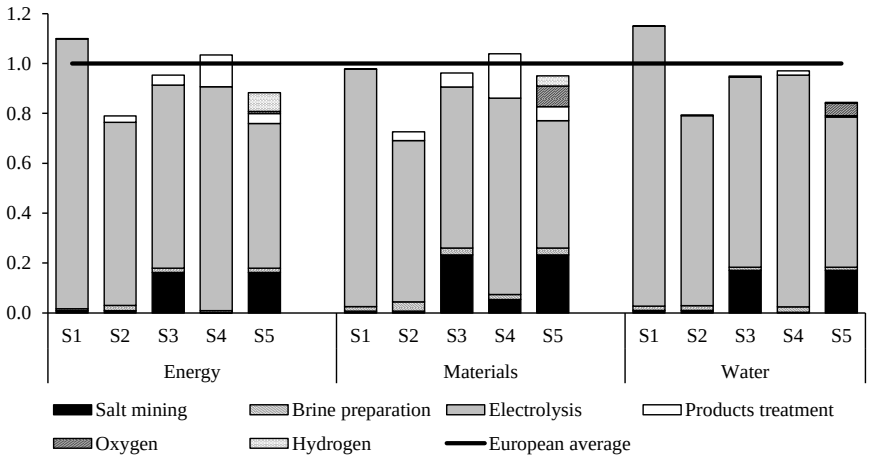

Fig. 2 Comparison of the NR dimensionless variables with regard to the European reference for the scenarios under study. S1: mercury technology; S2: membrane technology using salt sourced from KCl waste and 3 effects evaporation for NaOH; S3: membrane technology using vacuum salt and 2 effects; S4: diaphragm technology; S5: ODC technology.

3.2 Environmental burdens

The EBs to air, water and land are displayed in Fig. 3-5. The results are divided into the four subsystems under study: salt mining, brine preparation, electrolysis and products treatment. The values are scaled to ease the comparison among the different impact categories.

Similar to NR, mercury technology (S1) presents the highest burdens for the majority of air categories owing to the energy demand of the electrolytic stage (Fig. 3). It is followed by diaphragm technique (S4), which involves on average 10% lower environmental impacts. The exception is GW, for which S4 results the worst scenario due to the lower purity of NaOH product delivered by diaphragm technique.

When the best available technology based on a standard cathode is compared to the emergent technique based on an oxygen-depolarised cathode, several issues must be addressed. Being both technologies compared under same conditions (S3 and S5), the emergent technology is the most environmentally sustainable. This difference, which is much lower than the 30% expected (Moussallem et al., 2008), is on average 13% and much lesser for GW. In particular, the GW of S3 and S5 are 2.75 and 2.68 kg CO_2-eq, respectively. In contrast, Jung et al. (2014), estimated those values at 2.28 and 2.1 kg CO_2-eq, respectively. The reason of this reduction in the GW values may lie in the modelling of salt extraction, since vacuum salt is assumed in this work and a generic model from Ecoinvent is used in Jung et al. (2014). Similar conclusions are obtained from Kätelhön et al. (2015), although results are not directly comparable since another functional unit and methodology are used in that study.

Regarding stage contributions, the electrolytic stage is still the main responsible of the EB to air, accounting on average for more of the 85% of the environmental impacts. This contribution is higher in AA, HHE and SOD categories due to the emission of SO_2

and halogenates from electricity generation. A lower share is particularly observed for S5, as opposed to the production of hydrogen by steam reforming considered by system expansion.

On the other hand, the contribution of salt production and brine preparation can involve until 20% of the total impacts, depending on the salt source considered. The importance of such stages was already remarked in Hong et al. (2014), where sodium chloride production was responsible for more than a fifth of the environmental impacts of caustic soda production. In particular, vacuum salt is the less sustainable option due to the electricity demand for vacuum salt production by means of mechanical steam recompression, accounting for 18% of the total EB to air in S3 and S5. Conversely, the impact of KCl waste and solution mining is almost negligible due to the low energy demand of their extractions. In this sense, the substitution of vacuum salt (S3) by KCl waste (S2) involves a 16% reduction of the environmental impacts. Such percentage reflects the different environmental sustainability levels that can be obtain as a results of process stage decisions on the best available technology. The contribution of NaOH concentration is on average 3.5%. Despite being higher for GW (7.5%) owing to the CO_2 emissions from the burning of natural gas for steam production, the difference between using 2 or 3 effects evaporation is below 2%. Finally, the contribution of brine preparation itself remains below 5% for every air category.

Similar energy related conclusions can be applied to the results obtained for water categories. However, while the process for brine preparation is not relevant for air impact categories, it emerges as the second main hotspot together with salt mining. In particular, the largest impact of brine preparation is observed for S4, since the quantity of brine treated in once-through systems is higher than in close systems and thus reactants requirements and solid waste generation are the largest. This effect is specially

observed for AqA category (21%), mainly due to the inorganic emissions to water (HF) caused by the landfill of solid wastes. Brine preparation contribution is also significant in S1, S2 and S4 for AOD category (10%), due to the water emissions of organic compounds (methanol) in the production of Na_2CO_3. The impact of this step is almost negligible for vacuum salt (S3 and S5), since the main precipitation process is conducted before evaporation. No data have been found in the literature regarding EB to water from these stages, excepting for Hong et al. (2014), where around 30% of environmental impacts to water compartment are due to NaCl extraction by well drilling.

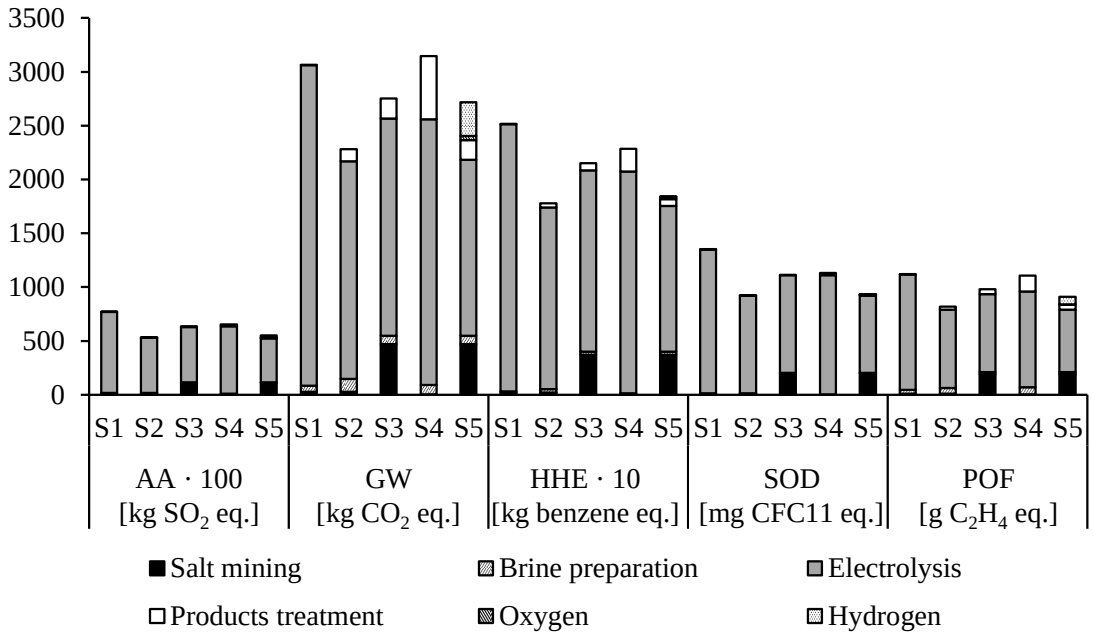

Fig. 3 EB to air for the scenarios under study. The values for some impacts have been scaled to fit on the scale. The original values can be obtained by dividing the scores shown on the y-axis by the scaling factor given on the x-axis. All the impacts are expressed per mixed ton of the electrochemical unit. Impact categories: AA: atmospheric acidification; GW: global warming; HHE: human health (carcinogenic) effects; SOD: stratospheric ozone depletion; POF: photochemical ozone formation.

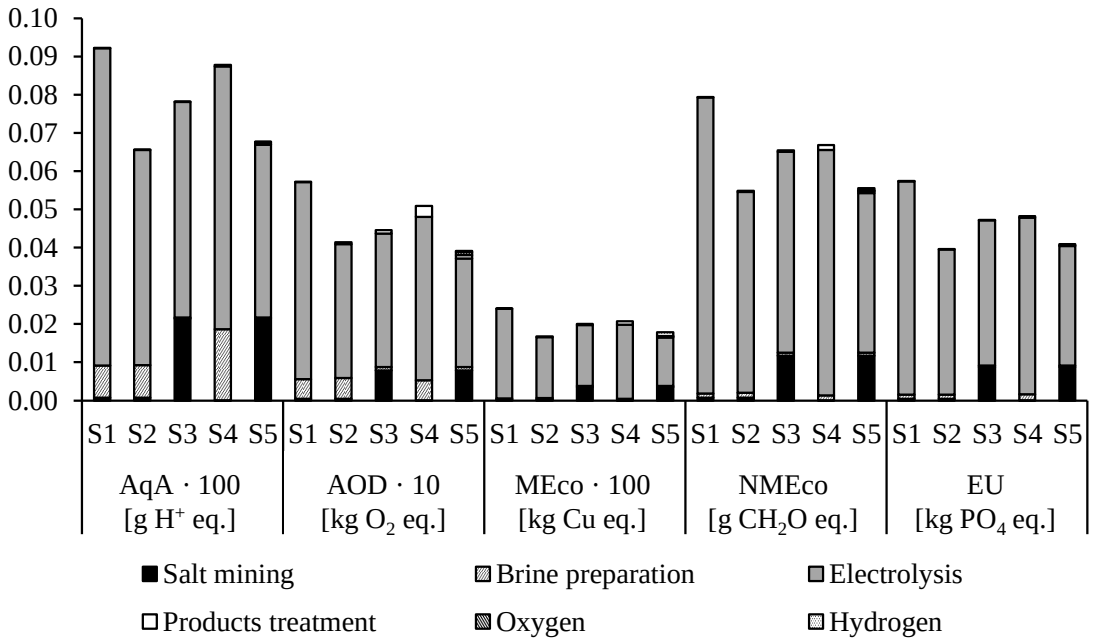

Fig. 4 EB to water. Impact categories: AqA: aquatic acidification; AOD: aquatic oxygen demand; MEco: ecotoxicity to aquatic life (metals to seawater); NMEco: ecotoxicity to aquatic life (other substances); EU: eutrophication. The values for some impacts have been scaled to fit on the scale, as described in Fig. 3.

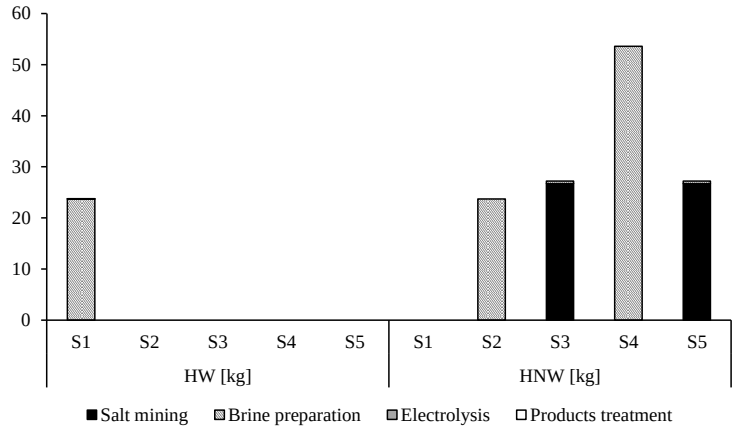

Fig. 5 EB to land. Impact categories: HW: hazardous waste; HNW: non-hazardous waste.

Regarding EBs to land, most of the solid waste are obtained in the brine preparation step (Fig. 5). This waste stream is non-hazardous for every scenario, except for S1. This is because the mercury content, which is also present in waste from hydrogen and

NaOH treatment processes. However, their amounts are negligible in comparison to the rest of waste streams. A significant quantity of waste is also produced in the salt mining stage for S3 and S5, due to the $CaCO_3$ and $Mg(OH)_2$ precipitates formation when vacuum salt is sourced from rock salt. None waste is obtained in solution mining process, although the precipitates are further delivered in the once-through brine preparation process.

The results obtained from these set of metrics provide the proper framework to discuss the contribution of the different stages and the best and worst scenarios for each category. However, the different units of the impact categories hinder the comparison across the different results of the scenarios under study. To go a step further, the environmental burdens are normalised using the PRTR threshold values. In this way, the values are adjusted to have common dimensions and thus they can be aggregated into the variables $X^*_{2,1}$, $X^*_{2,2}$ and $X^*_{2,3}$, which describes the EBs to air, water and land in Fig. 6.

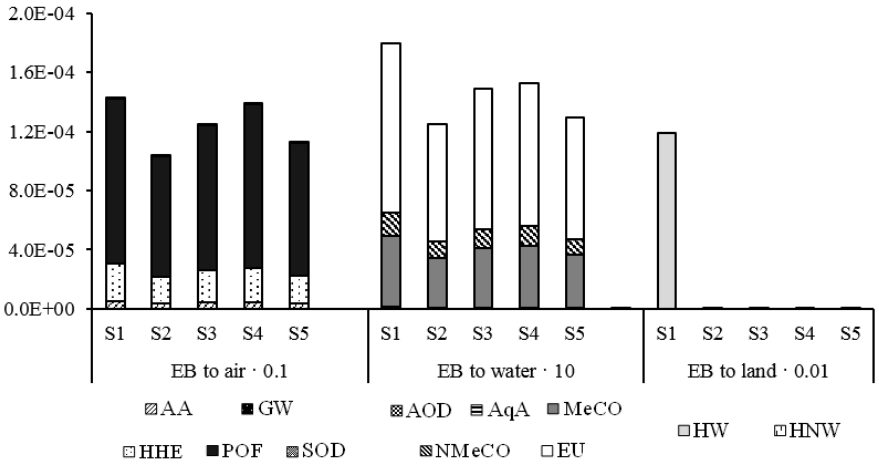

Fig. 6 Dimensionless EB to air, water and land for the scenarios under study. The contribution of the different impact categories to each EB are shown. The values have been scaled to fit on the y-axis, as explained in Fig. 3.

After normalisation, POF followed by HHE become the most important EBs to air. Consequently, the difference between S1 and S4 is softened to 3%. The emergent scenario involves lower EB to air than S3, although this difference is less than 10%. On the other hand, S2 achieves a 20% reduction with regard to S3. The main contributors to $X^*_{2,2}$ are EU and MeCO. S1 presents significant higher impacts to water than the rest of technologies, achieving a 15% difference with the second worst scenario (S4). Regarding EB to land, it must be remarked that hazardous waste from S1 is the most notably burden, resulting negligible the impact generated to the rest of scenarios.

The environmental impacts studied are aggregated, as shown in Table 3, into two composite indexes: NR and EB, described by variables X_1 and X_2. These values are used to classify the scenarios according to their environmental impacts intensity in Fig. 7. Values near the symbol "+" indicate the largest impacts. Consequently, S1 is the worst performing scenario, followed by S4, and both NR and EB agree with this classification. While in terms of NR S1 related impacts are nearly 6% higher than those from S4, EB value from S1 is around 9 times higher than the corresponding to S4. The hazardous waste from mercury cell technique are the main responsible to this difference. Under same conditions, the emergent technique (S5) is the most environmentally sustainable technology, achieving a 9% reduction in the environmental impacts with regard to S3. On the other hand, a higher reduction is observed when S3 is compared to S2 (18%). Therefore, the best scenario is S2, followed closely by S5 since, similar results are obtained for EB index, for which the main contributor is $X^*_{2,1}$. Conversely, a major discrepancy is observed in NR, owing to the materials requirements for the emergent technology.

Table 3 NR and EB dimensionless variables for the scenarios under study. Colour coding is used to reflect environmental impacts intensity. Higher impacts are coloured in red, while lower impacts are coded with green.

		Scale	S1	S2	S3	S4	S5
Energy	$X^*_{1,1}$	1	1.10	0.79	0.95	1.03	0.88
Materials	$X^*_{1,2}$	1	0.98	0.73	0.96	1.04	0.95
Water	$X^*_{1,3}$	1	1.15	0.79	0.95	0.97	0.84
NR	$\mathbf{X_1}$	**1**	**1.07**	**0.77**	**0.96**	**1.01**	**0.89**
EB to air	$X^*_{2,1}$	10^{-3}	1.42	1.03	1.24	1.38	1.13
EB to water	$X^*_{2,2}$	10^{-5}	1.80	1.25	1.49	1.52	1.29
EB to land	$X^*_{2,3}$	10^{-3}	11.89	0.01	0.01	0.03	0.01
EB	$\mathbf{X_2}$	$\mathbf{10^{-3}}$	**13.33**	**1.06**	**1.27**	**1.42**	**1.15**

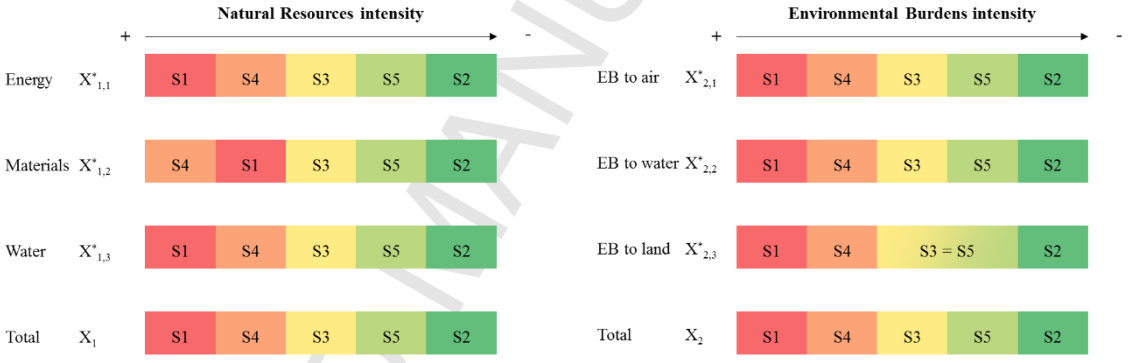

Fig. 7 Intensity of the Natural Resources (NR) consumption and Environmental Burdens (EB) generated. Higher intensity values are to left in each diagram

3.3 Allocation procedure

3.3.1 Mass allocation

Inputs to the system related to raw materials, electricity and steam are mass allocated to the products leaving the system. Steam requirements cannot be merely assigned to sodium hydroxide concentration, as some plants claim a significant steam use in other stages. The distribution of electric energy among the different chlor-alkali products has

been a topic of discussion over the last years. Several approaches have been proposed, but no general agreement has been reached (Boustead, 2005).

In particular, the mass allocation factors were estimated in a previous work (Garcia-Herrero et al., 2017) according to the production values of 1 ton of chlorine, 1.128 tons of sodium hydroxide (100%) and 28.5 kg of hydrogen. Since NaOH is considered to be produced as a 50% solution, the generation of 2.256 tons of 50% NaOH was assumed to mass factor calculation. As hydrogen production is below 1%, its contribution was excluded from the analysis applying a cut rule.

As can be observed in Table 4, the majority of the impacts are attributed to NaOH, which is responsible for 70% of the environmental profile of the chlor-alkali process. The rest is assigned to chlorine production.

Table 4 NR and EB dimensionless variables for chlor-alkali products using mass allocation

	Scale	S1	S2	S3	S4	S5
Chlorine						
NR (X_1)	0.1	3.30	2.36	2.93	3.12	2.74
EB (X_2)	10^{-3}	4.09	0.32	0.39	0.44	0.35
Sodium hydroxide						
NR (X_1)	0.1	7.45	5.33	6.62	7.03	6.19
EB (X_2)	10^{-3}	9.24	0.73	0.88	0.99	0.80

3.3.2 Economic allocation

Economic allocation is usually based on the market value of products. However, this approach does not consider the technology under study. Consequently, although no substantial modification is produced in the technique, economic allocation may lead to significant varied results due to economic fluctuation over time. This effect is clearly

depicted by the chlor-alkali industry, where chlorine and caustic soda prices have dramatically fluctuated over the last thirty years. For example, chlorine and sodium hydroxide prices were both around 125€/ton in 1970, while in 1984 they were 135€ and 252€ per ton of chlorine and sodium hydroxide, respectively. Therefore, the economic allocation factor under these circumstances decreased from 50% to 35% for chlorine, while it rose from 50% to 65% for sodium hydroxide. In 1986, the economic factors of both products became similar again (≈50%), to be reverted in 1990 to 38% and 62% for chlorine and sodium hydroxide, respectively. As the technological changes in the chlor-alkali industry were few those years, the production features should remain practically constant. However, allocation procedure in terms of economic values involves significant uncertainties due to the cyclic and changeable nature of the market.

Economic allocation factors were estimated in a previous work (Garcia-Herrero et al., 2017) taken into account the 2006-2011 market reference price for chlorine, sodium hydroxide and hydrogen (Eurostat 2013).

As can be observed in Table 5, similar contribution (69%) is obtained for NaOH when considering economic allocation. As opposed to mass allocation, the environmental impacts related to hydrogen are not negligible when the economic variable is analysed. The reason lies in the higher market price of hydrogen (1.697 €/kg) than chlorine (0.165 €/kg) and NaOH (0.224 €/kg). In this case, the remaining 31% contribution is shared between hydrogen and NaOH, being the allocation factor of NaOH lower than in the previous procedure (23% vs. 30%). The NR and EB dimensionless results according to economic allocation are shown in Table 5.

Table 5 NR and EB dimensionless variables for chlor-alkali products using economic allocation

Scale	S1	S2	S3	S4	S5
Chlorine					
NR (X_1)	0.1	2.47	1.77	2.20	2.33	2.05
EB (X_2)	10^{-3}	3.07	0.24	0.29	0.33	0.27
Sodium hydroxide					
NR (X_1)	0.1	7.56	5.41	6.72	7.14	6.28
EB (X_2)	10^{-3}	9.37	0.74	0.89	1.00	0.81
Hydrogen					
NR (X_1)	0.1	0.72	0.52	0.64	0.68	0.60
EB (X_2)	10^{-3}	0.89	0.07	0.09	0.10	0.08

4. Conclusions

This work develops an exhaustive and multifunctional Life Cycle Assessment (LCA) model to describe the European chlor-alkali sector and further assess the environmental sustainability of the process and the integration opportunities of emergent technologies in the sector. The model integrates all the stages present in the production process, including the production of salt as raw material, the main configurations for brine preparation, the treatment of products and the management of the waste generated. Mercury, diaphragm, membrane and oxygen-depolarised cathode (ODC) are the four technologies under study.

Considering the chlor-alkali industry under a life cycle approach, the majority of the environmental impacts are related to energy consumption. In this sense, the major contributing stage is the electrolytic process, which is responsible on average for 85% of the total natural resources consumption (NR) and environmental burdens (EB) to air, water and land. Consequently, mercury technique is the less environmentally sustainable option, whose environmental profile is also aggravated by the inherent presence of mercury in its emissions. Diaphragm technology emerges as the second worst scenario

owing to the penalisation of the NaOH concentration process, which constitutes its main hotspot after electrolysis. The reason lies in the low purity NaOH (12% vs 50%) delivered by this technique.

Therefore, membrane technique, which has been labelled as the best available technology for chlor-alkali production, is the best performing technology industrially implemented. Its environmental profile can even be improved when the standard hydrogen evolution cathode is replaced by an oxygen depolarised cathode (ODC), which constitutes the emergent technology. Despite reducing the electricity consumption, the competitive advantage of ODC (S5) versus membrane scenario (S3) is reduced to 8%, as opposed to the 30% reported in the literature. The integration of this technology in the market is challenged by the lack of hydrogen production, which would be otherwise valorised as in the rest of scenarios.

Results of this work also show the high relevance of salt production, which can amount up to 20% of the total impacts, depending on the salt source considered. Owing to the high electricity demand of vacuum salt production, it constitutes the worst environmental salt production option, being the main hotspot of the chlor-alkali process, after electrolysis. Conversely, KCl waste constitutes the best environmental option, followed by solution mining. The contribution of brine preparation to the environmental impacts, can also involve up to 20%, especially in water and land impact categories owing to the precipitation reactants used and subsequent solid waste generated. This effect is more accused for diaphragm technology due to the once-through brine system.

On the other hand, this paper shows how the environmental sustainability of a technology can be significantly improved (or aggravated) by process decisions in other life cycle stages, besides the electrolytic step. Taken as reference membrane scenario, results demonstrated that the environmental profile can be reduced by up to 18% when

lower energy demanding processes for salt production and NaOH concentration were selected. This improvement percentage overcomes the estimated for standard cathodes replacement by ODC.

The technology developments and the innovation initiatives in the chlor-alkali sector are mainly aimed to increase the operational current densities in membranes, involving higher fluxes through membranes and higher brine quality requirements to maintain the membranes' lifetime. This model can help to lead the investment efforts not only to a change of electrolytic technology but also on a renewal or revamping of caustic soda concentration unit or on a deeper analysis of the brine purification system in order to allow new salt sources as raw material. Simultaneously, taking into account the tendency to promote and support projects for the sustainability of industrial processes, on-going work based on the development of a composite index could allow an objective and quantitative parameter to measure the plants situation, considering not only the environmental axis but also the economical one, closely linked with the competitiveness of European industry.

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